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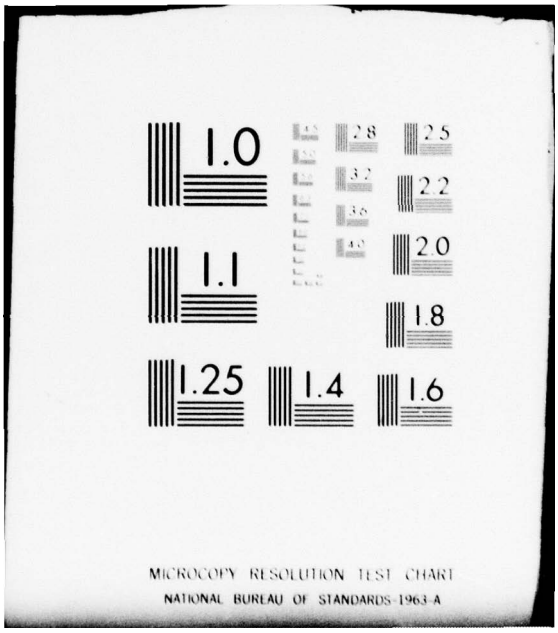
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FERROELECTRIC POLARIZATION IN POLYMERS

by

M. G. Broadhurst and G. T. Davis

Prepared for Publication

in the

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A cooperative model has been developed to describe ferroelectric polarization in polyvinylidene fluoride (PVDF). The molecular dipoles within the crystal are assumed to have two or more orientations available to them and the lattice energy of a given orientational site is assumed to be proportional to the fraction of molecules having that orientation. An analytical solution is given for the 2-site model which predicts polarization hysteresis typical of ferroelectrics. However, a more complex 6-site model, which can be analysed

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numerically, is needed to account for observed infra red hysteresis data and electric-field-induced x-ray structural changes which have been reported for PVDF. Although the model is simple, rather complex behavior is observed including a gradual increase or decrease in the remnant polarization with number of cycles of electric field application. Though the agreements with various experimental data are good an obvious need to include kinetic effects in the model is indicated.

FERROELECTRIC POLARIZATION IN POLYMERS

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INTRODUCTION

Previous work has shown that a model of oriented dipoles accounts quite well for observed piezoelectric and pyroelectric behavior of amorphous[1] and semicrystalline[2] polymers. The process whereby the dipoles become oriented is the subject of this paper. Here we summarize a model and calculated results for ferroelectric reorientation of molecular dipoles in the all-trans polar crystal phase (β phase or Form I) of polyvinylidene fluoride. By ferroelectric we mean a material with polar crystals where the polarization direction can be reversed with an applied electric field.

In the model, the orientations of molecular dipoles depend on the electric field and the history of the field application. The quantities $\langle\cos\theta\rangle$, $\langle\cos^2\theta\rangle$, and $f(\theta)$ can be calculated where θ is the angle between a dipole and the applied field, $f(\theta)$ is the fraction of dipoles at angle θ and the brackets $\langle\rangle$ indicate a spacial average. The experimental physical quantities of interest for comparison with the model are polarization (a measure of $\langle\cos\theta\rangle$), infra red transmission intensity[3,4] (a measure of $\langle\cos^2\theta\rangle$) and x-ray pole figure data[5] (a measure of $f(\theta)$). Since only one adjustable parameter is used in the model, these various comparisons permit an unusually thorough evaluation of the strengths and weaknesses of the model.

THE MODEL

Polyvinylidene fluoride (PVDF) is a linear molecule with a carbon backbone. In its crystalline forms the molecule has a large moment normal to the chain.

In the β crystal phase the unit cell is polar and the crystals form lamellae typically 10 nm thick with the molecular segments nearly normal to the large crystal surfaces.[2] The molecular segments which traverse the crystal lamellae are interconnected through the intercrystalline amorphous regions (See Fig. 1) either by tight folds at the lamellar surface or by longer irregular molecular segments. As demonstrated in the data referenced later in this paper, the segments in the crystal can rotate as rigid rods or by a propagating twist mechanism about their chain axis, giving a reorientation of the crystal moment. The shape of the curve relating potential energy to angle for individual chain rotation is not known, but following Kepler and Anderson's observation that the near-hexogonal unit cell cross section will permit a six-fold degeneracy in the orientation of the crystal,[5] we assume equivalent potential energy minima, 60 degrees apart as shown in Fig. 2. The potential energy of an orientation θ_i relative to a base line is U_i and the fraction of segments having that orientation is f_i. We use the first order, mean field cooperativity assumption[6,7] that $U_i = -U_0 f_i$ where U_0 is the energy difference between a filled and empty site. This assumption describes the desired feature that if most segments have a given orientation then that orientation is the preferred one (having the lowest energy). The lattice energy of the crystal is given by $\Sigma U_i f_i = -U_0 \Sigma f_i^2$, the dipole-field interaction energy is given by $-m_0 E \Sigma f_i \cos\theta_i$ (where the field is assumed to be at 0 degrees), and the entropy is given by $-k\Sigma f_i \ell n f_i$. We do not include dipole-dipole interactions. The Helmholtz free energy is

$$(A_i - A_0) = -U_0 \Sigma f_i^2 - m_0 E \Sigma f_i \cos\theta_i + kT \Sigma f_i \ell n f_i \qquad (1)$$

We can minimize the free energy including the constraint that $\Sigma f_i = 1$ by using a Lagrange multiplier technique. That is, we solve the equations,

$$\partial(A_i - A_0)/\partial f_j - \lambda \partial(\Sigma f_i)/\partial f_j = 0. \qquad (2)$$

The result is a set of 6 equations

$$-2U_o f_i - m_o E \cos\theta_i + kT(1 + \ell n f_i) - \lambda = 0 \qquad (3)$$

We can solve the simple 2 site case analytically[8] but this 6 site example must be solved numerically as detailed elsewhere.[9]

RESULTS

The result of the calculation is that at E = 0 for $U_o/kT > 2.0118$ (an unusual type of Curie point for this model), the 6-fold-degenerate lowest energy solution is for one site to be heavily populated and the remaining five sites to have lesser (but equal to each other) populations. At $|E| > 0$, the degeneracy is removed and depending on E and the angle between E and a preferred site, a particular distribution may become unstable and a new distribution form resulting in a change in the magnitude and direction of the crystal moment. The assumed mode of redistribution of orientations is somewhat arbitrary but the one giving results closest to experiment assumes that once a site i is unstable, the probability that, of the remaining stable sites, site j will be favored is proportional to $\exp(m_o E \cos\theta_j/kT)$. This assumption is not to be confused with the equilibrium assumption of Kepler and Anderson[5] that the population of site j will be proportional to this term. In our case the orientations are not at equilibrium and are highly dependent on the initial distribution of orientations and history of electric field application.

The numerical calculation is done by varying $m_o E/kT$ in equation 3 (after dividing by kT) by small increments, recomputing f_i and if a given solution is unstable, redistributing the f_i as described above. We assumed an initial distribution of crystals such that the crystal moments and applied field are in the plane of the crystal lamellae and the moments are equally distributed every 10 degrees from 0 to 350 degrees. From the record of f_i versus E we calculate $\langle\cos\theta\rangle$, $\langle\cos^2\theta\rangle$ and the fraction of reflecting crystal planes at

angle θ_i as a function of field and history. To compare m_0E/kT to the applied field we assume a molecular segment in the crystal is 10 nm long. Such a segment contains 40 repeat units of 6.9×10^{-30} Cm vacuum moment each. The reaction field (in the spherical approximation) enhances this moment by $(\epsilon_c + 2)/3 \sim 5/3$ giving a total segment moment of 4.6×10^{-28}Cm. Thus, a 1 MV/cm field at room temperature gives $m_0E/kT = 11$. This value is well above the range of linear dielectric response typically encountered with molecular dipoles. We used a lattice energy of $U_0/kT = 3$ for our calculations which gives a critical field (for which the first crystals switch) of about 1 MV/cm. Remembering the U_0 is the energy difference between an empty and filled site, we see that the dipole-field energy can be much greater than the crystal energies. Reducing U_0/kT to 2.5 reduces the critical field by half but as a function of reduced field, E/E (critical), the calculations are insensitive to U_0/kT. For simplicity, we have ignored kinetic effects in the calcultaions even though they are inherent in the model. For example, thermodynamic fluctuations will allow a crystal to switch to a new preferred orientation at fields below the critical value and all redistributions of dipoles involve rotations which encounter local energy barriers - a process which takes time.

COMPARISON WITH EXPERIMENT

The calculated polarization as a function of electric field through 1½ cycles is shown in Figure 3. Experimental curves obtained by cycling the field at a constant rate of change[10] are shown in Figure 4. Both the observed critical switching field and degree of polarization (as a fraction of the total possible polarization) are satisfactorily mimicked by the calculated curve. The quantity $m_0E/kT = 11$ corresponds to E = 1 Mv/cm for 10 nm thick crystals and for these mixed phase samples (30% α crystals, 30% β crystals and 40% amorphous phase) the maximum polarization will be about 10 $\mu C/cm^2$. To account for the reversible permittivity of the amorphous phase we have added a relative permittivity of 15 to the model which accounts for the slope in curves of Fig. 3 upon decreasing the field.

Figure 5 is a comparison between calculated $\langle\cos^2\theta\rangle$ for the model and the measured hysteresis of the 512 cm^{-1} IR absorption in PVDF[3]. This absorption is due to β phase crystal vibrations polarized parallel to the CF_2 dipole moment. Random orientation of single axes rotators with the axes in the plane of the film corresponds to $\langle\cos^2\theta\rangle$ = 0.5 and 23% transmission. Complete alignment corresponds to $\langle\cos^2\theta\rangle$ = 1.0 and 40% transmission and these values are used to match the magnitudes of the ordinates. Thus the magnitudes and general positions of the two curves are very similar.

In Figure 6 we show calculated and observed x-ray pole figure results obtained at zero field after the material has been subjected to a polarization treatment. The abscissa refers to the angle between the bisector of the incident and diffracted x-ray beams and the normal to the PVDF film (or equivalently the direction of the poling field). The results from the present calculation (dashed curve) predict the correct magnitudes at zero and large angles and are less satisfactory than the equilibrium calculation[5] (solid line) at small angles.

While the above results support a conclusion that the essential features of the high field polarization in PVDF are described by a simple cooperative ferroelectric model, the curvature in the experimental hysteresis curves (Figs. 4 and 5) at zero fields is an obvious feature which has not been delineated in the present calculations.

ACKNOWLEDGEMENT

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REFERENCES

1. F. I. Mopsik and M. G. Broadhurst, J. App. Phys. 46, 4204 (1975).

2. M. G. Broadhurst, G. T. Davis, J. E. McKinney and R. E. Collins, J. Appl. Phys. 49 4992 (1978).

3. D. Naegele and D. Y. Yoon, Appl. Phys. Lett. 33, 132 (1978).

4. E. Fukada, M. Date and T. Furekawa, Organ. Coatings Plast. Chem. 38, 262 (1978). (Preprints for ACS Meeting in Anaheim Calif., 1978).

5. R. G. Kepler and R. A. Anderson, J. Appl. Phys. 49, 1232 (1978).

6. W. L. Bragg and E. J. Williams, Proc. Ray. Soc. A 145, 699 (1934).

7. W. P. Mason, Phys. Rev. 72, 854 (1947).

8. M. G. Broadhurst and G. T. Davis, in Topics in Modern Physics - Electrets, G. M. Sessler, Ed. Springer-Verlag, in Press.

9. M. G. Broadhurst and G. T. Davis, intended for J. Appl. Phys.

10. Data of A. DeReggi and S. C. Roth, at NBS.

FIGURE CAPTIONS

Figure 1. Structure of semicrystalline polyvinylidene fluoride showing lamellar crystals with molecular segments normal to the lamellae.

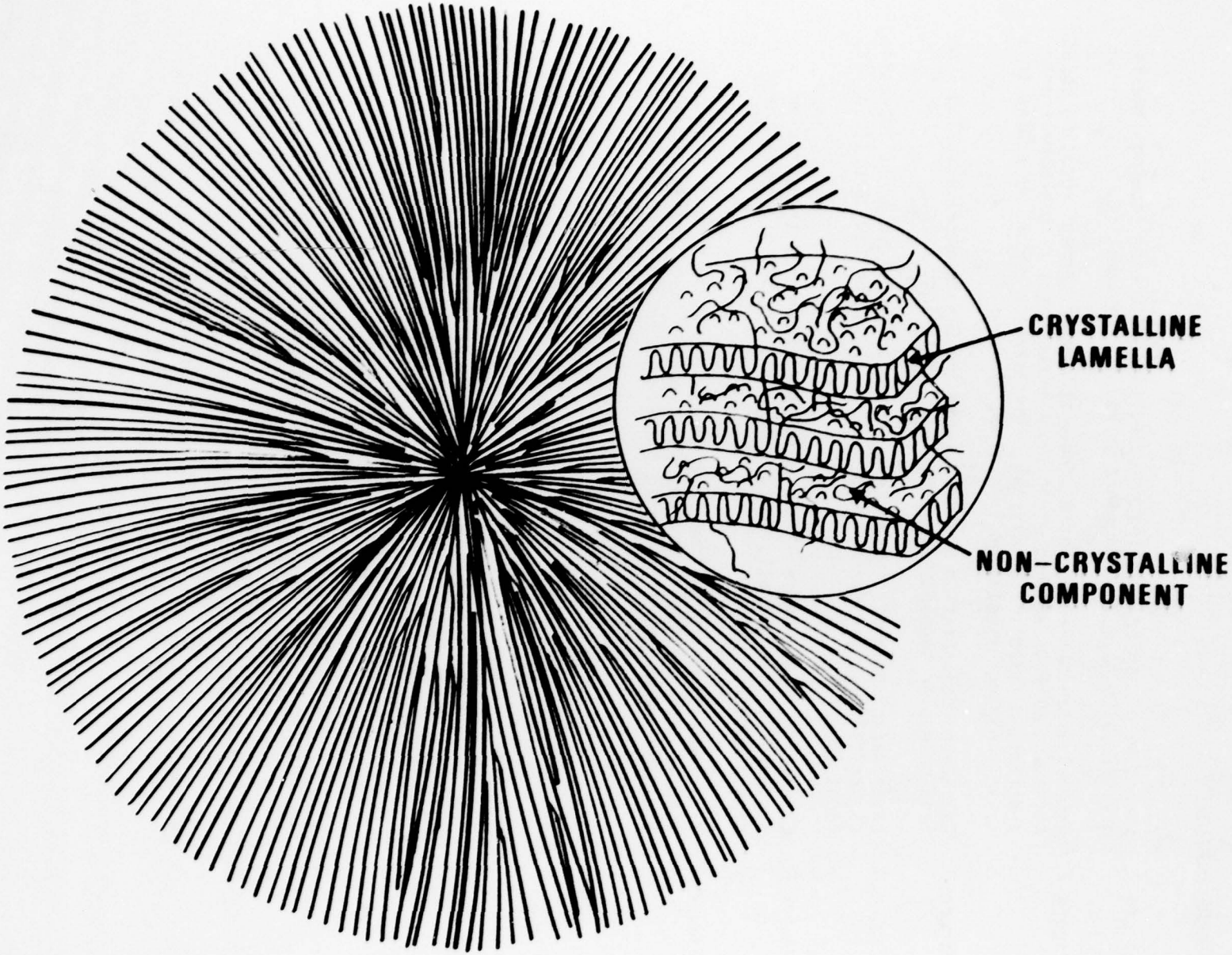
Figure 2. Assumed potential energy of a single molecular segment rotating about its chain axis as a function of angle between its dipole moment and a direction fixed in the crystal. The fraction of all molecules in a crystal having orientation i is given by f_i.

Figure 3. Calculated polarization hysteresis for the 6-site model assuming 10nm long molecular segments rotating about their long axis.

Figure 4. Experimental polarization hysteresis for a sample cycled at increasingly higher fields. The maximum residual polarization (at zero field) is about $10\mu C/cm^2$.

Figure 5. Experimental (Reference 3) and calculated infra red transmission hysteresis for a vibration polarized along the CF_2 dipole in the δ crystal phase.

Figure 6. X-ray pole figure data from Reference 5 (error bars) and calculated results from the 6-site ferroelectric model (dashed line) and an equilibrium distribution (solid line).



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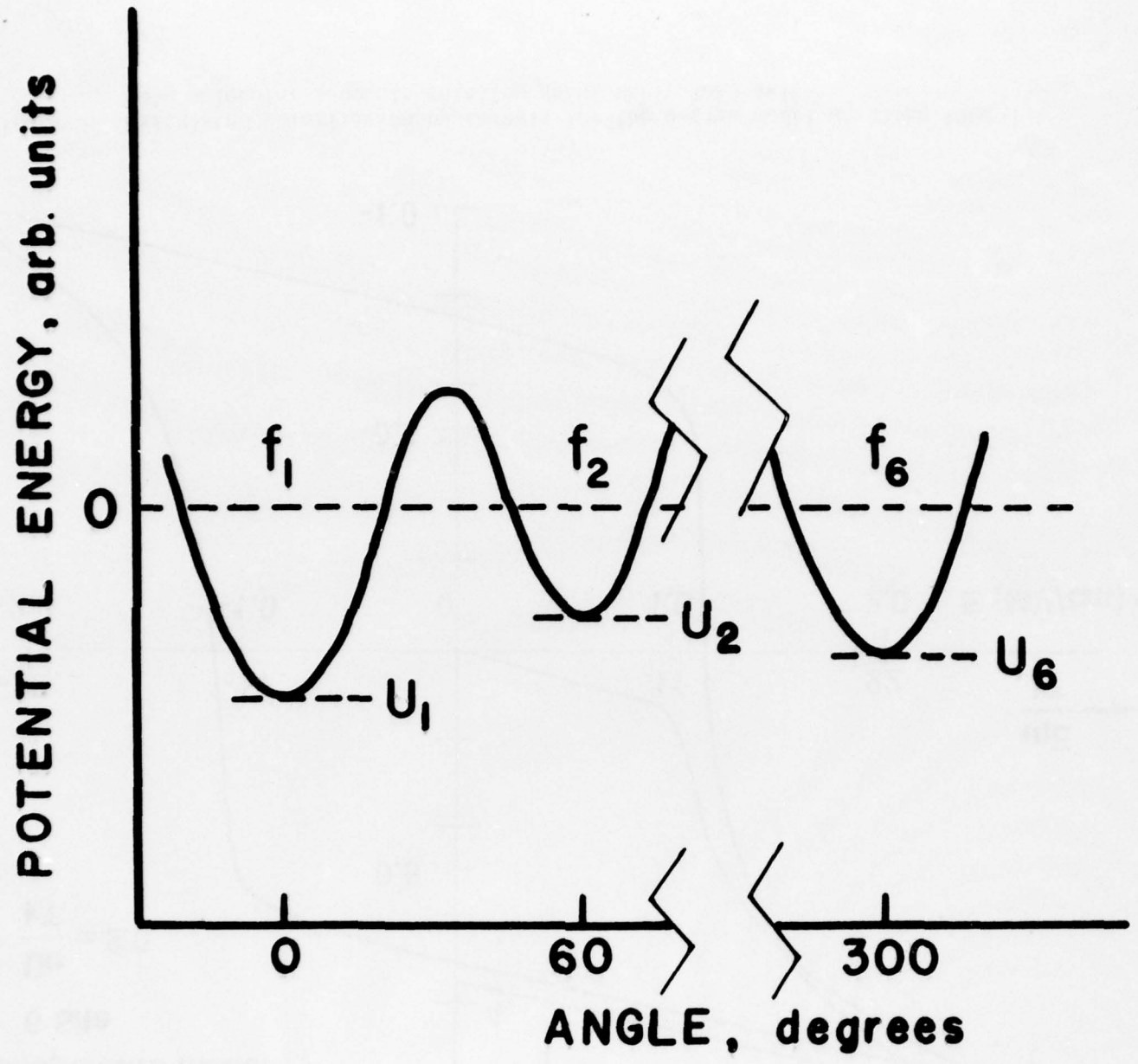


Figure 2. Assumed potential energy of a single molecular segment rotating about its chain axis as a function of angle between its dipole moment and the electric field direction. The fraction of all molecules in a crystal having orientation i is given by f_i.

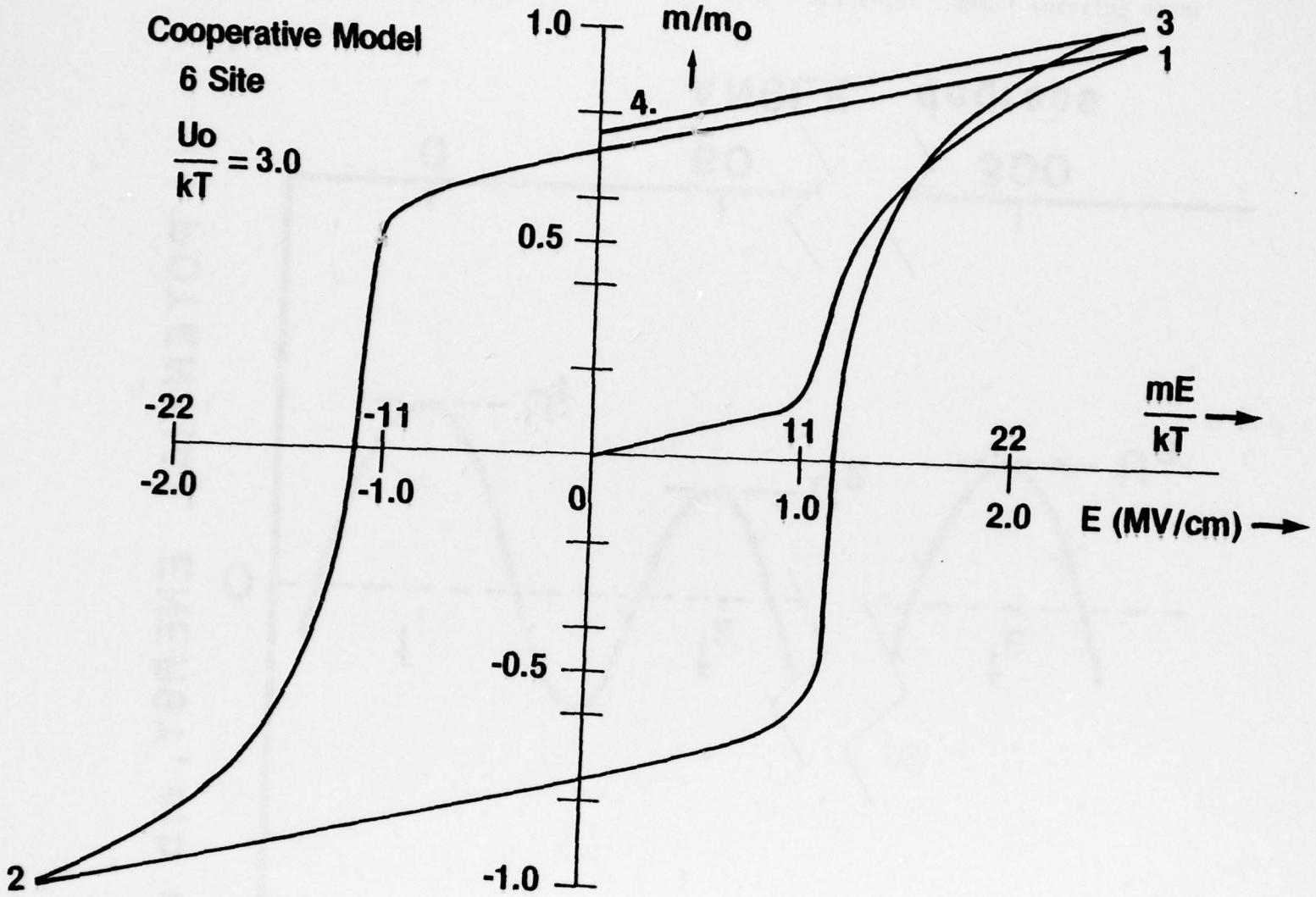
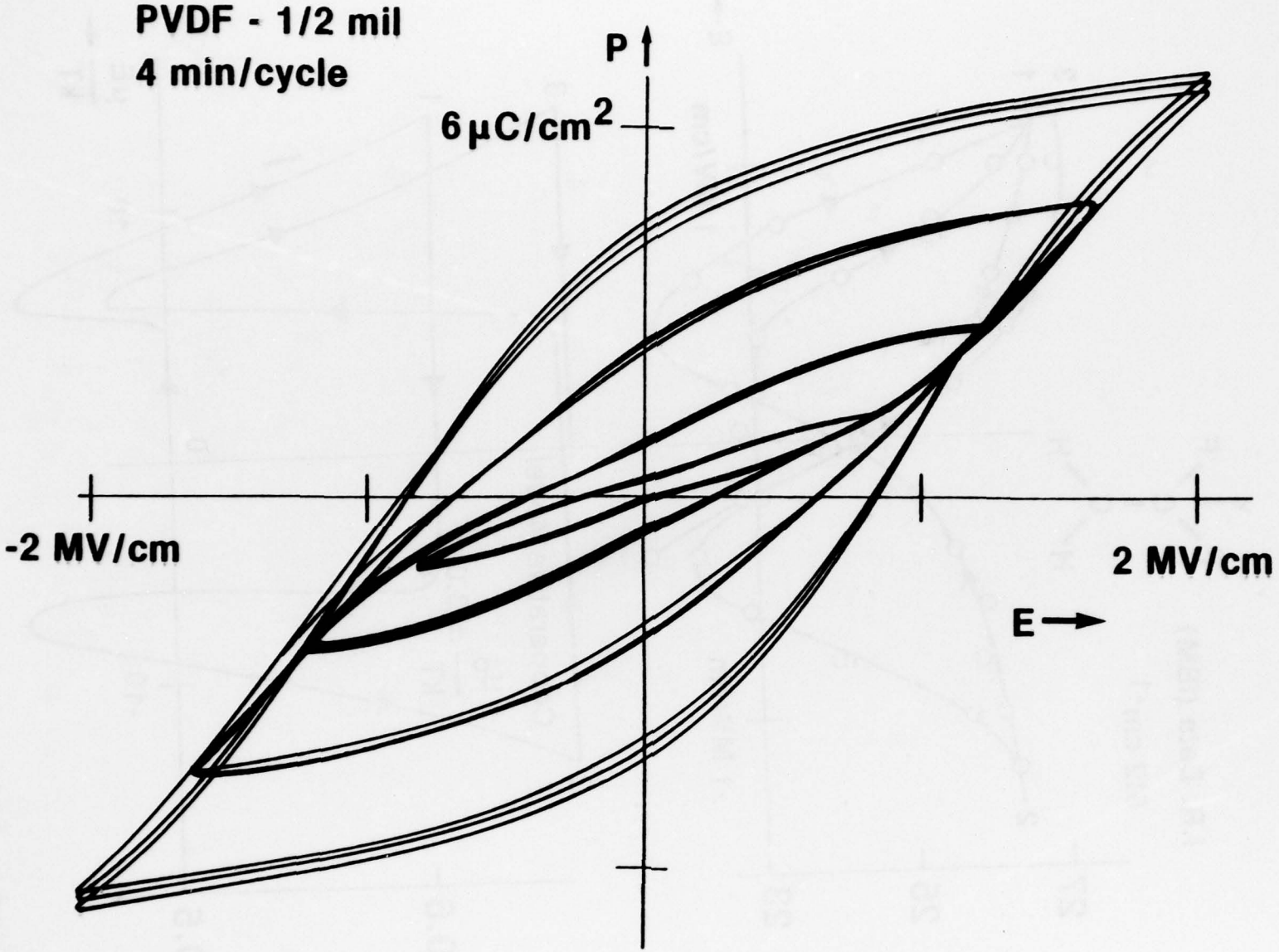


Figure 3. Calculated polarization hysteresis for the 6-site model assuming 10nm long molecular segments rotating about their long axis.



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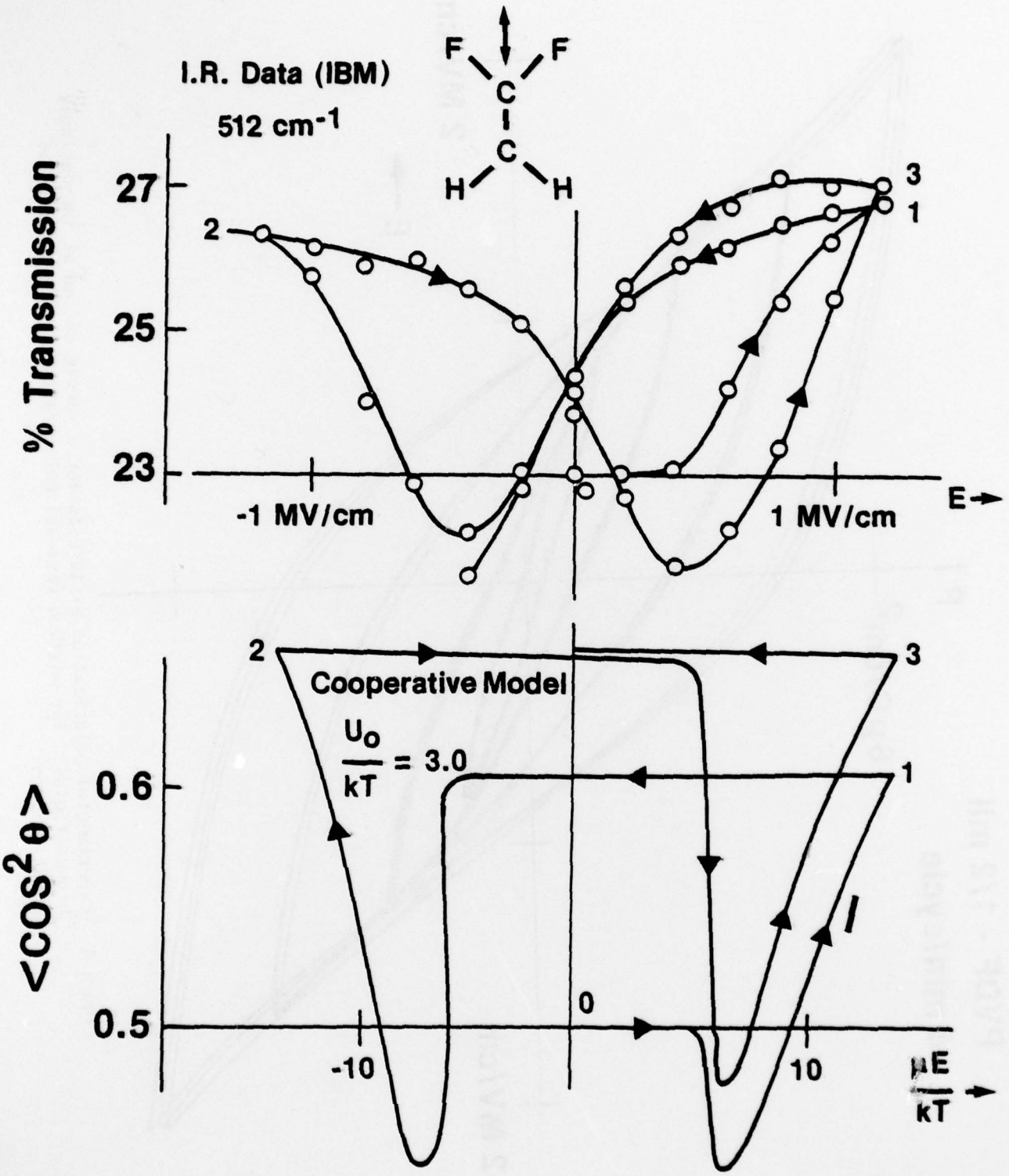

Figure 5. Experimental (Reference 3) and calculated infra red transmission hysteresis for a vibrational polarized along the CF_2 dipole in the β crystal phase.

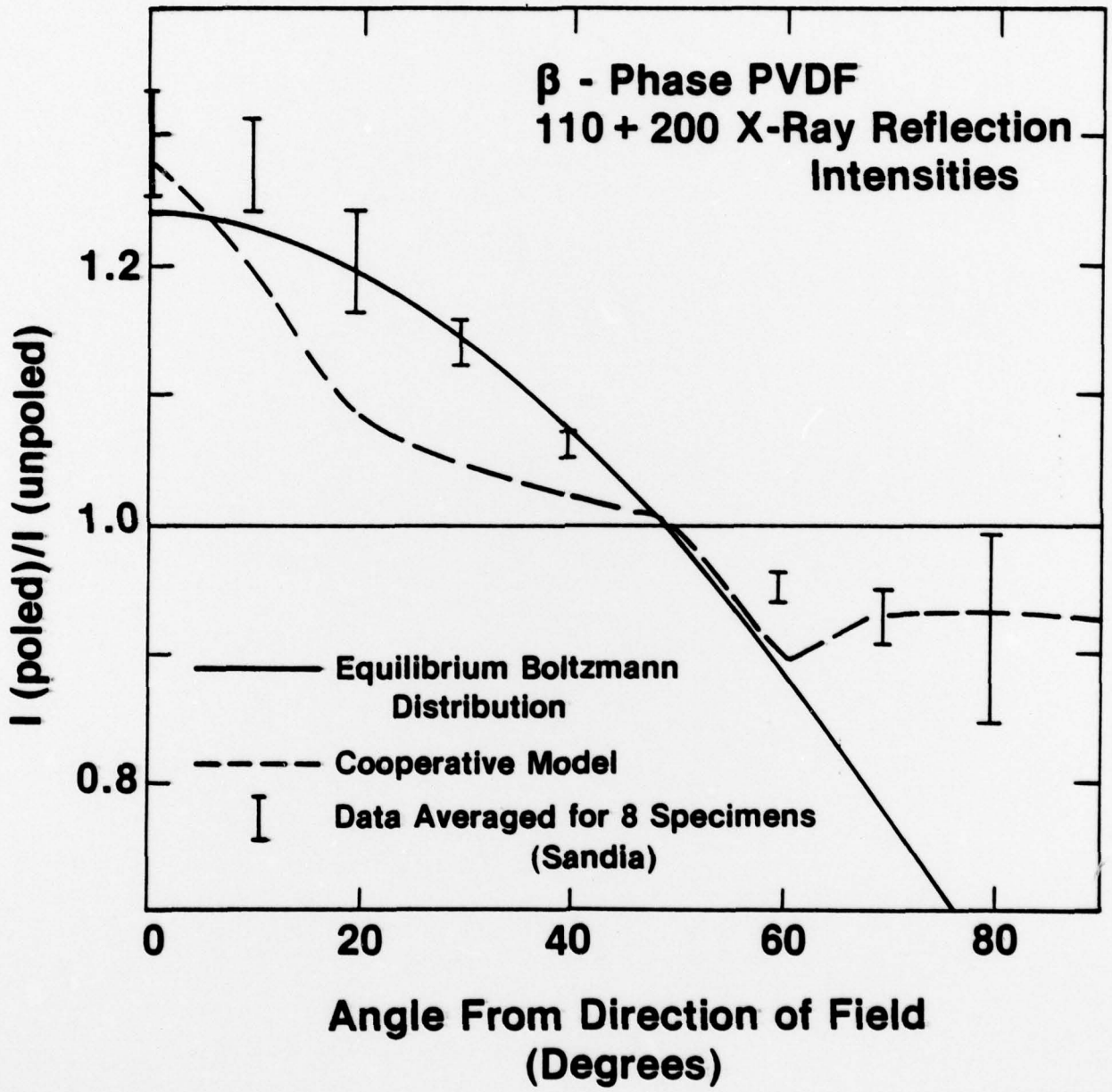

Figure 6. X-ray pole figure data from Reference 5 (error bars) and calculated results from the 6-site ferroelectric model (dashed lines) and an equilibrium distribution (solid line).

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